

PTO 17 JUN 2005

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29 JANUARY 2004 29-01-04

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THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

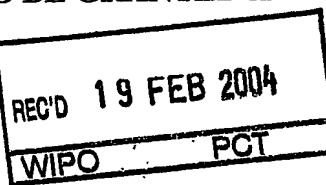
United States Patent and Trademark Office

December 08, 2003

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APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A  
FILING DATE UNDER 35 USC 111.

APPLICATION NUMBER: 60/433,967

FILING DATE: December 18, 2002



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**PROVISIONAL APPLICATION FOR PATENT COVER SHEET**

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

jc806

12/18/02

96-11-967 PRO

Express Mail Label No. 

INVENTOR(S)		
Given Name (first and middle [if any]) S Abdelhamid	Family Name or Surname Sayari	Residence (City and either State or Foreign Country) Ottawa, Canada

 Additional inventors are being named on the \_\_\_\_\_ separately numbered sheets attached hereto**TITLE OF THE INVENTION (500 characters max)**

Modified Adsorbent for Dry Scrubbing and Use Thereof

Direct all correspondence to:

**CORRESPONDENCE ADDRESS** Customer Number

28410



OR

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 Firm or Individual Name28410  
PATENT TRADEMARK OFFICE

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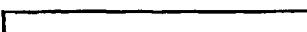
Fax

**ENCLOSED APPLICATION PARTS (check all that apply)** Specification Number of Pages

19

 CD(s), Number Drawing(s) Number of Sheets

8

 Other (specify) Application Data Sheet. See 37 CFR 1.76**METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT** Applicant claims small entity status. See 37 CFR 1.27.

FILING FEE AMOUNT (\$)

 A check or money order is enclosed to cover the filing fees

50-0548

\$80.00

 The Commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number: Payment by credit card. Form PTO-2038 is attached.

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

 No. Yes, the name of the U.S. Government agency and the Government contract number are: \_\_\_\_\_

Respectfully submitted,

SIGNATURE

TYPED or PRINTED NAME Jeffrey I. Auerbach

TELEPHONE (301) 896-0600

Date 12/18/2002

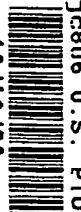
REGISTRATION NO.  
(if appropriate)  
Docket Number:

32,680

03515.101

**USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT**

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, Washington, D.C. 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Box Provisional Application, Assistant Commissioner for Patents, Washington, D.C. 20231.

12/18/02  
  
 JC806 U.S. PTO

12-18-02/PRO

## Fee Transmittal for FY 2002

Application No:	To Be Accorded
Filing Date	December 18, 2002
First Named Inventor	Abdelhamid SAYARI
Examiner Name	--
Group Art Unit	--

Total Amount of Payment **\$ 80.00**

Attorney Docket No. **03515.101**

Method of Payment				Fee Calculation (continued)																																																																																																																																																																																																																																																											
1. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge to Deposit Account No. <u>50-0548</u> [Account Name: Liniak, Berenato, Longacre & White, LLC]: <input type="checkbox"/> all indicated fees; <input checked="" type="checkbox"/> any additional fee required under 37 CFR 1.16 and 1.17; <input checked="" type="checkbox"/> Applicant claims SMALL ENTITY Status				<b>Additional Fees</b> <table border="1"> <thead> <tr> <th>Fee Code</th> <th>Large Entity Fee</th> <th>Fee Code</th> <th>Small Entity Fee</th> <th>Fee Description</th> <th>Fee Paid</th> </tr> </thead> <tbody> <tr><td>105</td><td>130</td><td>205</td><td>65</td><td>Surcharge late filing fee or oath</td><td></td></tr> <tr><td>127</td><td>50</td><td>227</td><td>25</td><td>Surcharge late prov. filing fee</td><td></td></tr> <tr><td>139</td><td>130</td><td>139</td><td>130</td><td>Non-English Specification</td><td></td></tr> <tr><td>147</td><td>2,520</td><td>147</td><td>2,520</td><td>Request for Reexamination</td><td></td></tr> <tr><td>112</td><td>920</td><td>112</td><td>920</td><td>Publ. of SIR prior to Exmr. action</td><td></td></tr> <tr><td>113</td><td>1,840</td><td>113</td><td>1,840</td><td>Publication of SIR after to Exmr. action</td><td></td></tr> <tr><td>115</td><td>110</td><td>215</td><td>55</td><td>Extension for Reply 1 Month</td><td></td></tr> <tr><td>116</td><td>400</td><td>216</td><td>200</td><td>Extension for Reply 2 Months</td><td></td></tr> <tr><td>117</td><td>920</td><td>217</td><td>460</td><td>Extension for Reply 3 Months</td><td></td></tr> <tr><td>118</td><td>1,440</td><td>218</td><td>720</td><td>Extension for Reply 4 Months</td><td></td></tr> <tr><td>128</td><td>1,960</td><td>228</td><td>980</td><td>Extension for Reply 5 Months</td><td></td></tr> <tr><td>119</td><td>320</td><td>219</td><td>160</td><td>Notice of Appeal</td><td></td></tr> <tr><td>120</td><td>310</td><td>220</td><td>155</td><td>Filing a Brief in support of Appeal</td><td></td></tr> <tr><td>121</td><td>270</td><td>221</td><td>135</td><td>Request for oral hearing</td><td></td></tr> <tr><td>138</td><td>1,510</td><td>138</td><td>1,510</td><td>Initiate Public Use Proceeding</td><td></td></tr> <tr><td>140</td><td>110</td><td>240</td><td>55</td><td>Petition to Revive Unavoidable</td><td></td></tr> <tr><td>141</td><td>1,280</td><td>241</td><td>640</td><td>Petition to Revive Unintentional Utility Issue Fee</td><td></td></tr> <tr><td>142</td><td>1,240</td><td>242</td><td>620</td><td></td><td></td></tr> <tr><td>143</td><td>440</td><td>243</td><td>220</td><td>Design Issue Fee</td><td></td></tr> <tr><td>144</td><td>600</td><td>244</td><td>300</td><td>Plant Issue Fee</td><td></td></tr> <tr><td>122</td><td>130</td><td>122</td><td>130</td><td>Petitions to the Commissioner</td><td></td></tr> <tr><td>123</td><td>50</td><td>123</td><td>50</td><td>Processing Fee (37 CFR 1.17(q))</td><td></td></tr> <tr><td>126</td><td>180</td><td>126</td><td>180</td><td>Submission of IDS</td><td></td></tr> <tr><td>581</td><td>40</td><td>581</td><td>40</td><td>Assignment Recordation</td><td></td></tr> <tr><td>146</td><td>710</td><td>246</td><td>355</td><td>1.129(n) Submission</td><td></td></tr> <tr><td>149</td><td>710</td><td>249</td><td>355</td><td>Add'l inventions to be examined</td><td></td></tr> <tr><td>179</td><td>710</td><td>279</td><td>355</td><td>Request for Continued Examination</td><td></td></tr> <tr><td>169</td><td>900</td><td>169</td><td>900</td><td>Expedited Exam. 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Submitted By	Jeffrey I. Auerbach	Reg. No. 32,680	Telephone	(301) 896-0600
Signature				Date <b>18-Dec-2002</b>

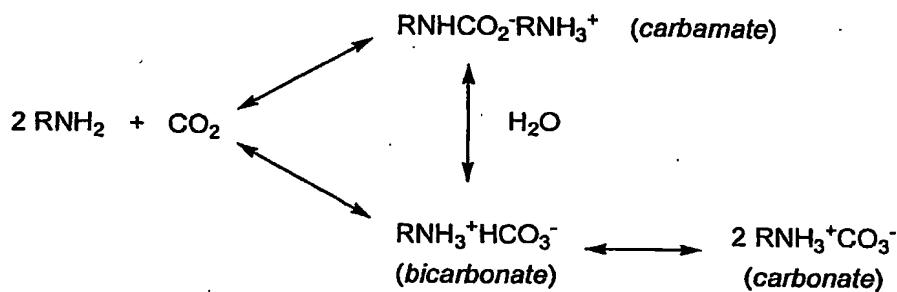
### FIELD OF THE INVENTION

The present invention pertains to the field of adsorbents and more particularly to the field of amine modified adsorbents for use in dry scrubbing processes.

### BACKGROUND

5 The use of gas scrubbing processes for environmental protection or for manufacturing of chemicals is widespread in industry (A. Kohl and R. Nielsen, "Gas Purification", Chap. II, Gulf Publ. Co, TX, USA, 1997). Removal of various gaseous pollutants such as volatile organic compounds (VOC), NO<sub>x</sub>, SO<sub>x</sub>, HF, HCl, H<sub>2</sub>S, CO<sub>2</sub>, phosphine and arsine often takes place via wet scrubbing, typically in countercurrent towers using either pure solvents (e.g., water or oil) or  
10 solvents containing dissolved materials which may consist of bases (D. Thomas and J. Vanderschuren, *Chem. Eng. Tech.* 23 (2000) 449; H. Bai and A.C. Yeh, *Ind. Eng. Chem. Res.* 36 (1997) 2490), salts (S. Lynn, A.L. Schiozer, W.L. Jaecksch, R. Cos and J.M. Prausnitz, *Ind. Eng. Chem. Res.* 35 (1996) 4236) or oxidants (T.J. Overcamp, *Environ. Sci. Technol.* 33 (1999) 155; U.S. Patent No. 5,527,517; T.W. Chien and H. Chu, *J. Hazard. Mater.* 80 (2000) 43). There are  
15 also "semi-dry" scrubbing processes using a slurry of solid particles which react with targeted species in the gas phase, ideally in a spray tower (D. Eden and M. Luckas, *Chem. Eng. Technol.* 21 (1998) 1). Dry scrubbing of gaseous acids using finely divided solid sorbents such as calcium oxide, hydroxide or carbonate in a cyclone reactor was also found, at the laboratory scale, to be highly efficient, particularly when partial recirculation of the solid reactant is achieved (A.M.  
20 Fonseca, J.J. Orfao and R.L. Salcedo, *Ind. Eng. Chem. Res.* 40 (2001) 304).

Carbon dioxide scrubbing is currently used on a large scale for the purification of industrial gases (natural gas, syngas, etc.) and also in life support systems in confined space (submarines, space shuttle and other inhabited engines for space exploration). These processes use mainly alkanolamine aqueous solutions (G. Astarita, D.W. Savage and A. Bisio, *Gas Treating with Chemical Solvents*, John Wiley, NY, 1983), the most common being mono- and diethanolamines, (MEA and DMEA) and N-methyldiethanolamine (MDEA). The process is reversible and can be represented as follows:



These reactions being exothermic, the formation of carbamate and bicarbonate is

5 favoured at low temperature, while their dissociation to amine and  $\text{CO}_2$  prevails at high temperature. The formation of one carbamate molecule requires two amine molecules, while a one-to-one ratio is required for bicarbonate. To maximise the  $\text{CO}_2$  adsorption capacity, it is therefore important to either enhance the hydrolysis of carbamate or limit its formation.

In addition to the decreased capacity due to carbamate formation, the use of aqueous

10 solutions of low molecular weight alkanolamines suffers a number of drawbacks (R.J. Hook, *Ind. Eng. Chem. Res.* 36 (1997) 1779; A. Veawab, P. Tontiwachwuthikul and A. Chakma, *Ind. Eng. Chem. Res.* 38 (1999) 3917); under scrubbing conditions, (i) a fraction of the amine and its decomposition products is lost by evaporation, which in addition to reducing the absorption capacity, may cause problems because of their toxicity, (ii) the amine undergoes oxidative

15 degradation leading to decreased capacity, increased viscosity and excessive foaming, (iii) excessive corrosion takes place, thus posing severe operational problems.

Introduction in the mid-eighties of the so-called sterically hindered amines by Exxon (G. Sartori and D.W. Savage, *Ind. Eng. Chem. Res.* 22 (1983) 239) mitigated these problems to a great extent. Indeed, these amines were less corrosive, less volatile, and the corresponding

20 carbamates were highly unstable. Actually, the most promising sterically hindered amine, namely 2-amino-2-methyl-1-propanol (AMP) does not yield any carbamate upon interaction with  $\text{CO}_2$  at low temperature (A.K. Chakraborty, G. Astarita and K.B. Bishoff, *Chem. Eng. Sci.* 41 (1986) 997). However, hindered amines exhibit lower rates of  $\text{CO}_2$  absorption. The use of high-efficiency column internals such as structural packing, or high surface area membranes leads to

improved mass transfer coefficients which compensate, at least partly, for the intrinsic low reactivity.

Dry scrubbing offers a viable alternative to the use of aqueous solutions. The use of dry scrubbing will reduce the amount of corrosion that occurs during the scrubbing process and the 5 acute problems related to the disposal of large amounts of contaminated wastewater will also be eliminated. Only limited examples of dry scrubbing studies exist; mostly dealing with absorption of acid gases by hydrated lime. In this case, there is incomplete utilisation of the adsorbent because of the increasing barrier of diffusion within the adsorbent particles. In addition to liquid phase systems that make use of amines, there have been attempts to use solid amines, 10 particularly for air revitalisation in manned space shuttles. Two recent patents disclose the use solid impregnated amines for cyclical adsorption of CO<sub>2</sub> (U.S. Patent Nos. 5,376,614 and 5,876,488).

A need remains for an adsorbent material for use in dry scrubbing processes that exhibits high capacity for acid gas adsorption and high acid gas adsorption rates.

15 This background information is provided for the purpose of making known information believed by the applicant to be of possible relevance to the present invention. No admission is necessarily intended, nor should be construed, that any of the preceding information constitutes prior art against the present invention.

20

#### SUMMARY OF THE INVENTION

An object of the present invention is to provide a modified support for dry scrubbing and use thereof. In accordance with an aspect of the present invention, there is provided an adsorbent comprising an amine-functionalised mesoporous silica.

25 In accordance with another aspect of the present invention, there is provided a regenerable, water-tolerant adsorbent comprising an amine-functionalised mesoporous silica or organosilica.

In accordance with another aspect of the invention, there is provided a regenerable adsorbent comprising an amine-functionalised mesoporous silica for use in dry scrubbing, wherein the mesoporous silica contains amine groups that are covalently bound to the surface of the silica.

5 In accordance with another aspect of the invention, there is provided a regenerable adsorbent comprising an amine-functionalised mesoporous silica for use in dry scrubbing, wherein the mesoporous silica has a hydrophobic surface and contains amine groups that are dispersed within the hydrophobic surface.

10 In accordance with another aspect of the invention, there is provided a regenerable adsorbent comprising an amine-functionalised mesoporous silica for use in dry scrubbing, wherein the mesoporous silica is prepared using amine-containing amphiphile molecules.

In accordance with another aspect of the invention, there is provided a regenerable adsorbent comprising an amine-functionalised mesoporous silica for use in dry scrubbing, wherein the mesoporous silica comprises an amine-functionalised framework.

15 In accordance with another aspect of the invention, there is provided a method of dry scrubbing comprising the step of contacting a gaseous stream containing an acid gas to be removed with a regenerable adsorbent comprising an amine-functionalised mesoporous silica.

#### BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a schematic view of the pore structure of a typical mesoporous silica.

20 Figure 2 depicts two general processes for the preparation of amine surface functionalised mesoporous silica.

Figure 3 depicts two general processes for the preparation of amine surface functionalised mesoporous silica via mesoporous silica that has been surface modified to contain non-amine reactive organic substituents.

25 Figure 4 depicts two general processes for the preparation of mesoporous silica containing supported amines.

Figure 5 depicts a general process for the preparation of hexagonal mesoporous silica (HMS) silica.

Figure 6 depicts two general processes for the preparation of amine-filled mesoporous silica using an amine-modified swelling agent.

5 Figure 7 depicts two general processes for the preparation of mesoporous silica containing an amine-functionalised framework.

10 Figure 8 is a schematic representation of a continuous CO<sub>2</sub> adsorption/desorption system comprising an adsorption column 1, a desorption column 2, a CO<sub>2</sub> monitor 3, a vacuum 6, a plurality of solenoid valves 7 and computer means 8 for control and acquisition. The input gas mixture is identified by reference number 4 and the purge gas by reference number 5.

#### DETAILED DESCRIPTION OF THE INVENTION

15 The present invention provides an amine functionalised adsorbent for use in dry scrubbing. The adsorbent comprises amine functionalised mesoporous organic-inorganic composites where all of the active functional groups (amines) are located inside the pore channels and/or within the pore walls and are readily accessible to the adsorbate. The configuration of the adsorbent of the present invention allows adsorption of acidic gases, including but not limited to CO<sub>2</sub> and H<sub>2</sub>S gas, at equivalent or higher rates, capacities and sensitivities than those obtainable using conventional liquid phase systems.

20 Since water is a ubiquitous impurity in gaseous streams, one embodiment of the present invention provides an adsorbent that has the additional characteristic of being water tolerant. The term "water tolerant," is used herein to indicate that the presence of moisture in the gas mixture does not hamper the adsorption of CO<sub>2</sub>, or other acidic gas, by the adsorbent. In a further embodiment of the present invention, the adsorbent has been designed to have the 25 additional characteristic of being capable of regeneration. The capacity for regeneration will allow the adsorbent to be used repeatedly, by first adsorbing the acid gas to be removed and subsequently stripping the adsorbent to free the amines for subsequent reuse.

### Components of Adsorbent

The adsorbents of the present invention can be prepared using various methods, including those outlined herein, in order to obtain material having varying capacities and rates of adsorption depending on the potential use of the material. In each case the adsorbent comprises 5 mesoporous silica or organosilica that has been modified to contain amines that are accessible to the adsorbate.

#### *Mesoporous silica*

Mesoporous silicas and organosilicas are prepared in the presence of surfactants or polymer solutions via different pathways including the so-called cooperative organization 10 mechanism (A. Firouzi, A. Monnier, L.M. Bull, T. Besier, P. Sieger, Q. Huo, S.A. Walker, J.A. Zasadzinski, C. Glinka, J. Nicol, D. Margolese, G.D. Stucky and B.F. Chmelka, *Science* 267 (1995) 1138) and the liquid crystal templating mechanism (G.A. Attard, J.C. Glyde and C.G. Göltner, *Nature* 378 (1995) 366). They may exhibit different structures and pore systems, the most prominent being the so-called MCM-41 with a two-dimensional hexagonal symmetry. Table 1 15 provides a non-limiting list of mesoporous silicas prepared under different pH conditions using different amphiphile molecules. The pore size of such material may be adjusted from a low of 1 nm to well into the macropore regime, i.e. > 50 nm (A. Sayari, M. Kruk, M. Jaroniec and I.L. Moudrakovski, *Advanced Materials*, 10 (1998) 1376; A. Sayari, Y. Yang, M. Kruk and M. Jaroniec, *J. Phys. Chem. B* 103 (1999) 3651; and A. Sayari, *Angewandte Chemie*, 39 (2000) 20 2920). They are thermally very stable and their surface area routinely exceeds 1000 m<sup>2</sup>/g. As shown in Figure 1, under proper hydration conditions, the inner surface which represents approximately 95% of the total surface is covered with OH groups that can be used to anchor a variety of surface modifiers. Comprehensive reviews on this subject are available in the literature (A. Stein, B.J. Melde and R.C. Schroden, *Adv. Mater.* 12 (2000) 1403 and A. Sayari and S. 25 Hamoudi, *Chem. Mater.*, invited review, 2001).

**Table 1**

Mesophase	Amphiphile template	pH	Structure	Reference
MCM-41	C <sub>n</sub> H <sub>2n+1</sub> (CH <sub>3</sub> ) <sub>3</sub> N <sup>+</sup>	basic	2D hexagonal ( <i>p6mm</i> )	[1]

Mesophase	Amphiphile template	pH	Structure	Reference
MCM-48	$C_nH_{2n+1}(CH_3)_3N^+$ Gemini $C_{n-s-n}^a$	basic	cubic ( $Ia\bar{3}d$ )	[1] [2]
FSM-16	$C_{16}H_{31}(CH_3)_3N^+$	basic	2D hexagonal ( $p6mm$ )	[3]
SBA-1	$C_{18}H_{37}N(C_2H_5)_3^+$	acidic	cubic ( $Pm\bar{3}n$ )	[2]
SBA-2	Divalent $C_{n-s-1}^b$	acidic	3D hexagonal ( $P6_3/mmc$ )	[2]
SBA-3	$C_nH_{2n+1}N(CH_3)_3^+$	acidic	2D hexagonal ( $p6mm$ )	[4]
SBA-6	Divalent $18B_{4-3-1}^c$	basic	cubic ( $Pm\bar{3}n$ )	[5]
SBA-8	Bolaform <sup>d</sup>	basic	2D rectangular ( $cmm$ )	[6]
SBA-11	Brij 56; $C_{16}EO_{10}$	acidic	cubic ( $Pm\bar{3}m$ )	[7]
SBA-12	Brij 76; $C_{18}EO_{10}$	acidic	3D hex. ( $P6_3/mmc$ )	[7]
SBA-14	Brij 30; $C_{12}EO_4$	acidic	cubic	[7]
SBA-15	P123; $EO_{20}PO_{70}EO_{20}$	acidic	2D hexagonal ( $p6mm$ )	[8]
SBA-16	F127; $EO_{106}PO_{70}EO_{106}$	acidic	cubic ( $Ia\bar{3}m$ )	[7]
FDU-1	B50-6600; $EO_{39}BO_{47}EO_{39}$	acidic	cubic ( $Ia\bar{3}m$ )	[9]
FDU-2	$RN^+N^+N^+^{(d)}$	basic	cubic ( $Fd\bar{3}m$ )	[10]
MSU-1	Tergitol; $C_{11-15}(EO)_{12}$	neutral	disordered	[11]
MSU-2	TX-114; $C_8Ph(EO)_8$ TX-100; $C_8Ph(EO)_{10}$	neutral	disordered	[11]
MSU-3	P64L; $(EO_{13}PO_{30}EO_{13})$	neutral	disordered	[11]
MSU-4	Tween-20, 40, 60, 80	neutral	disordered	[12]
MSU-V	$H_2N(CH_2)_nNH_2$	neutral	lamellar	[13]
MSU-G	$C_nH_{2n+1}NH(CH_2)_2NH_2$	neutral	lamellar	[14]
HMS	$C_nH_{2n+1}NH_2$	neutral	disordered	[15]
Mesocellular	P123 + TMB <sup>f</sup>	acidic	disordered	[16]

(a) Gemini surfactants  $C_{n-s-n}$ :  $C_nH_{2n+1}N^+(CH_3)_2(CH_2)_sN^+(CH_3)_2C_nH_{2n+1}$ .

(b) Divalent surfactants  $C_{n-s-1}$ :  $C_nH_{2n+1}N^+(CH_3)_2(CH_2)_sN^+(CH_3)_3$ .

(c) Divalent surfactant  $18B_{4-3-1}$ :  $C_{18}H_{37}O-C_6H_4-O(CH_2)_4N^+(CH_3)_2(CH_2)_3N^+(CH_3)_3$ .

(d) Bolaform surfactants : $(CH_3)_3N^+(CH_2)_nO-C_6H_4-C_6H_4-O(CH_2)_nN^+(CH_3)_3$ .

(e) Tri-head group surfactant:  $C_{16}H_{33}N^+(CH_3)_2(CH_2)_2N^+(CH_3)_2(CH_2)_3N^+(CH_3)_3$ .

5

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11. S.A. Bagshaw, E. Prouzet and T.J. Pinnavaia, *Science* 269 (1995) 1242.

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14. S.S. Kim, W. Zhang and T.J. Pinnavaia, *Science* 282 (1998) 1302.

15. P.T. Tanev and Pinnavaia, *Science* 267 (1995) 865.

16. P. Schmidt-Winkel, W.W. Lukens, Jr., D. Zhao, P. Yang, B.F. Chmelka and G.D. Stucky, *J. Am. Chem. Soc.* 121 (1999) 254.

15 Mesoporous silica is prepared using standard techniques (Table 1) known to those skilled in the art, for example, in the presence of alkyltrimethylammonium surfactants using literature procedures (A. Sayari, *Stud. Surf. Sci. Catal.* 102 (1996) 1-46). Different methods for pore size engineering can be used, including, but not limited to the use of auxiliary organic molecules such as trimethylbenzene, the post-synthesis treatment with long chain tertiary amines (A. Sayari, M.

20 Kruk, M. Jaroniec and I.L. Moudrakovski, *Advanced Materials*, 10 (1998) 1376; A. Sayari, Y. Yang, M. Kruk and M. Jaroniec, *J. Phys. Chem. B* 103 (1999) 3651; A. Sayari, *Angewandte Chemie*, 39 (2000) 2920) or the use of selected surfactants (R. Ryoo, et al., *J. Amer. Chem. Soc.* 123 (2001) 1650).

25 Following the initial preparation steps the mesoporous silica or organosilica may be calcined or extracted to remove surfactant and, if necessary, characterised using X-ray diffraction, N<sub>2</sub> adsorption, scanning electron microscopy, and/or transmission electron microscopy.

30 Mesoporous silicas or organosilicas that are suitable for use in the present invention exhibit high surface areas to enable high loading of adsorption sites, and provide sufficiently large pores to enable relatively unhindered flow of CO<sub>2</sub>, or other acid gas, containing gaseous streams inside the pore system.

### *Amines*

The amines used in the preparation of the adsorbent of the present invention must exhibit sufficient basicity to allow for efficient reaction with CO<sub>2</sub>, or other acidic acid to be adsorbed. In

addition a high N/C ratio can be beneficial to maximising the concentration of amine groups added to the mesoporous silica. In order to allow effective regeneration of the adsorbent, the amine should have relatively low volatility to ensure that the amine remains attached to the adsorbent during desorption processes.

5 The amines may be primary amines, secondary amines, tertiary amines, mixed amines or any combination thereof. Many suitable amines are commercially available. Other suitable amines may be synthesised using standard procedures.

Selection of the specific amine or amines to be used in the preparation of the adsorbent of the present invention will depend on the configuration of the adsorbent and on the application for 10 which the adsorbent is intended. For example, in cases where an high adsorptive capacity is not required then the amine or amines will be selected keeping in mind characteristics such as high regeneration ability, low cost and ready availability rather than maximum reactivity. In general, primary and secondary amines are more reactive with acidic gases than tertiary amines. Similarly, primary amines are generally more reactive than secondary amines.

15 **Synthesis of Adsorbent**

The use of various synthetic methods allows the production of adsorbents having different characteristics for use in diverse applications. Once prepared the adsorbent may be characterised in terms of pore structure and surface coverage using standard techniques.

*I. Amine surface functionalised mesoporous silica*

20 In accordance with one embodiment of the present invention the adsorbent is prepared such that the surface of the mesoporous silica is chemically modified to contain covalently attached amino groups.

1. Amine functionalised silica

25 In a specific embodiment of the present invention, following preparation of the mesoporous silica, surface functionalisation is performed by post-synthetic grafting of an amine-containing trialkoxysilane to the surface of the mesoporous silica as depicted in Figure 2.

Alternatively, surface functionalisation is achieved by direct synthesis through co-condensation of an amine-containing trialkoxysilane with tetraalkoxysilane, according to the co-condensation process generally depicted in Figure 2.

5 Table 2 provides a non-limiting list of amines that may be used in the preparation of the adsorbent of the present invention via post-synthesis grafting or via co-condensation (Figure 2).

Table 2

AMINE FORMULA	CHEMICAL NAME
<b>Primary Amines</b>	
NH <sub>2</sub> -(CH <sub>2</sub> ) <sub>3</sub> -Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	aminopropyltrimethoxysilane
NH <sub>2</sub> -(C <sub>6</sub> H <sub>4</sub> )-Si(OCH <sub>3</sub> ) <sub>3</sub>	p-aminophenyltrimethoxysilane
NH <sub>2</sub> -(C <sub>6</sub> H <sub>4</sub> )-O-(CH <sub>2</sub> ) <sub>3</sub> -Si(OCH <sub>3</sub> ) <sub>3</sub>	3(m-aminophenoxy)propyltrimethoxysilane
<b>Secondary Amines</b>	
CH <sub>3</sub> -NH-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -Si(OCH <sub>3</sub> ) <sub>3</sub>	N-methylaminopropyltrimethoxysilane
(C <sub>6</sub> H <sub>5</sub> )-NH-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -Si(OCH <sub>3</sub> ) <sub>3</sub>	N-phenylaminopropyltrimethoxysilane
<b>Tertiary Amines</b>	
(CH <sub>3</sub> ) <sub>2</sub> N-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -Si(OCH <sub>3</sub> ) <sub>3</sub>	N,N-dimethyl aminopropyltrimethoxysilane
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -Si(OCH <sub>3</sub> ) <sub>3</sub>	N,N-diethyl aminopropyltrimethoxysilane
[HO-(CH <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> N-(CH <sub>2</sub> ) <sub>3</sub> -Si(OCH <sub>3</sub> ) <sub>3</sub>	Bis(2-hydroxyethyl)3-aminopropyltrimethoxysilane
<b>Mixed Diamine</b>	
NH <sub>2</sub> -(CH <sub>2</sub> ) <sub>2</sub> -NH-(CH <sub>2</sub> ) <sub>3</sub> -Si(OCH <sub>3</sub> ) <sub>3</sub>	N-(2-aminoethyl)-3aminopropyltrimethoxysilane

2. Functionalised silica modified by amines

10 In an alternative embodiment of the present invention, the adsorbent is prepared using mesoporous silica that has been functionalised using a reactive organic substituent capable of amine modification. One example of a suitable organic group is an unsaturated carbon-carbon bond, which may be provided via a substituent such as vinyl, allyl, ethynyl and propargyl. The suitable reactive substituent may be introduced onto the surface of the silica using post-synthetic grafting procedures or through co-condensation using appropriate starting materials as illustrated  
15 in Figure 3.

## II. *Mesoporous Silica Containing Supported Amines*

In accordance with another embodiment of the present invention the adsorbent comprises amines that are supported on mesoporous silica having a hydrophobic surface. Suitable amines for use in the preparation of this adsorbent include, but are not limited to, alkylamines, such as 5 monoethanolamine (MEA), diethanolamine (DEA), diisopropylamine (DIP), N-methyldiethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP), polyethylenimine,  $\beta,\beta'$ -hydroxyaminoethylether and mixtures thereof. The hydrophobic silica is obtained via pore size expansion of any silica mesophase such as MCM-41, MCM-48, SBA-n, MSU-n, etc (Table 1) in the presence of a swelling agent followed by selective extraction of the swelling agent in the 10 presence of suitable solvents. The pore expansion may be carried out through direct synthesis in the presence of swelling agents such as long chain amines, hydrocarbons and trimethylbenzene, or via post-synthesis treatment in the presence of swelling agents such as N,N-dimethylalkylamines, as generally depicted in Figure 4.

15 Introduction of an amine-containing molecule to the expanded-extracted mesoporous silica results in the amine-containing molecule being dispersed on and within the hydrophobic surface of the pores of the silica.

## III. *Amine-filled mesoporous silica*

In accordance with an additional embodiment of the present invention, the adsorbent is prepared using standard procedures for the preparation of mesoporous silica in which one or 20 more of the reagents have been modified to contain reactive amino groups. A specific example of this embodiment is known as hexagonal mesoporous silica (HMS; P.T. Tanev and Pinnavaia, *Science* 267 (1995) 865) (Table 1), which is prepared using alkylamine as amphiphile molecule template. A diagrammatic representation of the HMS silica production is provided in Figure 5.

25 Another example of such an amine-filled mesoporous silica is referred to as amine-swollen silica (Type III-2 in Table 3). In this case the adsorbent is prepared using standard techniques in which the swelling agent has been modified to contain one or more type of reactive amino group. As shown in Figure 6, the amine-modified swelling agent may be used in a post-

synthetic swelling procedure or in a direct synthetic swelling procedure for the preparation of the amine-filled mesoporous silica.

#### *IV. Mesoporous organosilica with amine-functionalised framework*

In another embodiment of the present invention, the adsorbent is a mesoporous organosilica in which an organic functionality is incorporated into the framework of the silica. The raw material is a mesoporous organosilica of the general formula  $(1.5\text{OSi}-\text{R}-\text{SiO}_{1.5})$  with a suitable organic linker, R, such as an unsaturated carbon-carbon bond. Examples of such groups are ethylene and acetylene. For example, mesoporous ethylenesilica is prepared via condensation of bis-ethylenetriethoxysilane  $((\text{C}_2\text{H}_5\text{O})_3\text{Si}-\text{CH}=\text{CH}-\text{Si}(\text{OC}_2\text{H}_5)_3)$  in the presence of an amphiphilic molecule (Figure 7). This precursor can also be co-condensed with tetraethyl orthosilicate in any proportion. Subsequent reactions introduce as many amine functions as possible in order to maximise the adsorption capacity of the adsorbent, which is directly related to the number of amine groups per weight or volume unit of the final material. Similar adsorbents may be obtained via direct synthesis using amine-containing organosilica precursors (Figure 7).

#### Use of Adsorbent

The present invention further provides a method and a system for removing  $\text{CO}_2$  and/or other acid gases, such as  $\text{H}_2\text{S}$ , from a gaseous stream containing one or more of these gases.

Once the adsorbent has been formed, it can be employed in a sorbent bed where a gaseous stream containing  $\text{CO}_2$ , and possibly water, contacts the adsorbent. The  $\text{CO}_2$ , water and amine chemically react to form an amine complex, thereby removing the  $\text{CO}_2$  and water from the gaseous stream. According to a specific embodiment of the present invention, once the adsorbent is loaded with  $\text{CO}_2$  to a satisfactory level, when preferably greater than 80% of the amine has been converted to the amine complex, or at a designated cycle time, the sorbent bed can be regenerated. Regeneration comprises ceasing the flow of the gaseous stream through the bed and desorbing the adsorbed  $\text{CO}_2$  and water. The endothermic desorption reaction is accomplished by thermal and/or pressure gradient means or by the use of a sweeping or purge

gas. During this step, the amine complex is dissociated, CO<sub>2</sub> and water are removed and the amine is freed and ready for re-use.

It is understood that the adsorbent of the present invention is not limited to use for the removal of CO<sub>2</sub> from a gaseous stream. Rather the adsorbent can be used for the removal of any 5 acid gas, or combination thereof, from a gaseous stream, provided that the acid gas (or gases) is capable of reaction with amines.

In one embodiment of the present invention, use of the adsorbent to remove CO<sub>2</sub>, another acid gas, or a combination thereof, can comprise utilising two or more sorbent beds operating cyclically such that the first bed is in the adsorption cycle while the second bed is in the 10 desorption cycle. This allows for continuous CO<sub>2</sub> (or other acid gas) removal from the gaseous stream. In the adsorption cycle, an exothermic reaction occurs between CO<sub>2</sub> in the gaseous stream, which is flowing through the adsorbent, and the amine present in the adsorbent, thereby adsorbing the CO<sub>2</sub> and forming an amine complex. The heat produced during the adsorption process in the first bed can be transferred via a heat exchanger to the second bed to drive the 15 endothermic desorption of the adsorbed CO<sub>2</sub> and water simultaneously occurring therein. Alternatively, the desorption process can be effected through thermal and/or pressure gradient means independent of the adsorption process, or by the use of a purge gas.

In one embodiment of the present invention the adsorbent is used in conventional pressure or vacuum swing adsorption (PSA or VSA) systems. Gas separation by PSA is 20 achieved by coordinated pressure cycling and flow reversals over an adsorbent bed which preferentially adsorbs a more readily adsorbed component relative to a less readily adsorbed component of the mixture. The total pressure is elevated during intervals of flow in a first direction through the adsorbent bed from a first end to a second end of the bed, and is reduced during intervals of flow in the reverse direction. As the cycle is repeated, the less readily 25 adsorbed component is concentrated in the first direction, while the more readily adsorbed component is concentrated in the reverse direction. Figure 8 depicts an example of such a system, which is an automated, dual column PSA or VSA system.

Improved PSA systems allow the use of the adsorbent of the present invention in small, efficient CO<sub>2</sub> scrubbing units suitable for air revitalisation in confined spaces (e.g. space shuttles

and submarines). One example of an improved PSA system is based on the Pulsar™ technology developed by QuestAir Technologies (Burnaby, BC).

To gain a better understanding of the invention described herein, the following examples are set forth. It should be understood that these examples are for illustrative purposes only.

5 Therefore, they should not limit the scope of this invention in any way.

### EXAMPLES

#### **EXAMPLE 1: Preparation of Mesoporous Silica Adsorbent Containing Supported Amines**

Several samples of adsorbent according to the present invention were prepared using the 10 various techniques outlined herein.

One sample (SA -124) of adsorbent containing supported amine was prepared using 2 g of expanded-extracted MCM-41 material, which was added to a mixture containing 1 g of diethanolamine and 10 g of water. The mixture was stirred at room temperature for 2 hours and subsequently dried in an oven at 60°C for 40 hours. The resulting weight increase was 26.4% (2 15 g → 2.718 g).

A second sample (SA - 126) of adsorbent containing supported amine was prepared using the same procedure as described for the first sample, except that N-methyl-diethanolamine (1 g) was used in place of diethanolamine. The resulting weight increase was 17.3% (2 g → 2.345 g).

20 A third sample (SA - 127) of adsorbent containing supported amine was prepared using the same procedure as described for the first sample, except that the mixture contained 2 g of diethanolamine rather than 1 g. The resulting weight increase was 85% (2 g → 3.7 g).

25 A fourth sample (SA - 131) of adsorbent containing supported amine was prepared using the same procedure as described for the first sample, except that the mixture contained 3 g of diethanolamine rather than 1 g. The resulting weight increase was 125% (2 g → 4.5 g).

**EXAMPLE 2: Preparation of Amine Surface Functionalised Mesoporous Silica Adsorbent**

Synthesis of MCM-41 mesoporous silica (SA-117) was accomplished according to the following procedure: 68.325 g of CTAB was added to a mixture containing 48.1 g of TMAOH and 463.7 g of distilled water, after mixing under magnetic stirring for 30 min, 25 g of Cab-O-Sil (fumed silica) was added slowly to the solution. Stirring was maintained at room temperature for 1 h, the mixture was transferred into a Teflon-lined autoclave, which was heated to 100°C for 40 h. The MCM-41 material was obtained by filtration, washing by water, dried at ambient condition and calcination at 540°C for 5 h. The surface area of this material was: 1205 m<sup>2</sup>/g, the pore size 3.8 nm and the pore volume 1.2 cm<sup>3</sup>/g.

One sample (SA-117-amine) of amine surface functionalised silica was prepared using calcined MCM-41 (SA-117) as starting material. 5 g of SA-117 was heated in an oven at 120 °C for 2 h to eliminate moisture. In a three-necked flask, 100 ml of anhydrous toluene was refluxed under N<sub>2</sub> flow. Then the moisture-free MCM-41 was transferred into this flask under stirring and the mixture was kept under reflux. 2.41 g (0.013 mol) of aminopropyltrimethoxysilane (APTS) was added into this boiling mixture. The grafting procedure was maintained for 5 h. The powder was recovered by filtration, toluene-washing, and drying in air.

A second sample (SA – 128) of amine surface functionalised silica was prepared using 2 g of another calcined MCM-41 material (SA – 108), which was added to 100 ml toluene that contained 0.01 mol (2.22g) of N-[3-(trimethoxysilyl)propyl]-ethylenediamine. The mixture was stirred under reflux for 5 hours. The resulting solid was obtained by filtration and washed with toluene. The resulting weight increase was 34% (2 g → 2.68 g).

A third sample (SA – 129) of amine surface functionalised silica was prepared using the same method as SA-128, except that N,N-dimethylaminopropyltrimethoxysilane was grafted on the calcined MCM-41 rather than N-[3-(trimethoxysilyl)propyl]-ethylenediamine.

A fourth sample (SA – 130) of amine surface functionalised silica was prepared using the same method as SA-128, except that N-phenylaminopropyltrimethoxysilane was grafted on the calcined MCM-41 rather than N-[3-(trimethoxysilyl)propyl]-ethylenediamine.

The nitrogen content of all samples was determined experimentally using a EA1100 CHNS elemental analyzer.

**EXAMPLE 3: Measurements of CO<sub>2</sub> Adsorption Capacity**

Carbon dioxide adsorption data was obtained using a down-flow micro-reactor system  
5 connected to a gas chromatograph (GC) with a thermoconductivity detector (TCD). One gram of adsorbent was loaded in a glass reactor between two layers of glass wool. The sample was pre-treated in a constant N<sub>2</sub> flow (30 ml/min) at 100 °C for 3 hours before cooling to room temperature. A mixed gas comprising 3 % (v/v) CO<sub>2</sub> in nitrogen was allowed to flow through the sample bed (3 cm in height). After one minute, a small amount of the outlet gas was injected  
10 through a 6-way valve with a sample loop into the GC column. Sampling continued at one minute intervals until the material was saturated, i.e. no further adsorption of CO<sub>2</sub> observed.

In the early stages of testing, all CO<sub>2</sub> was adsorbed and the TCD did not detect any CO<sub>2</sub> in the outlet gas. As the adsorbent became saturated, more and more CO<sub>2</sub> was detected by the TCD, until the concentration of CO<sub>2</sub> detected by the TCD is equal to the concentration of CO<sub>2</sub> in  
15 the inlet gas. The total amount (adsorption capacity) of adsorbed CO<sub>2</sub> was then calculated.

Following the measurement of CO<sub>2</sub> adsorption capacity, the sample was regenerated to remove adsorbed CO<sub>2</sub> and thereby free the amine groups. This was accomplished by heating the CO<sub>2</sub>-loaded sample under nitrogen at 60 to 100 °C for 3 to 4 hours. In all cases, the amount of CO<sub>2</sub> adsorbed on regenerated and fresh adsorbents were comparable.

20 The effect of the presence of water in the gas stream was also investigated. In this case, the 3% CO<sub>2</sub>/N<sub>2</sub> mixture was passed through a water saturator before being allowed to flow through the adsorbent sample. The saturator temperature was maintained constant within a range of about 9 – 12 °C.

The results of these studies are summarised in Table 3.

Table 3

Sample	Type	Description	Activation or regeneration (°C)	V <sub>CO<sub>2</sub></sub> (ml/g)	CO <sub>2</sub> /N
blank		Calcined MCM-41	100	0	0
SA-50Ex	III-2	Expanded MCM-41	100	5.5	n.a.
SA-50EED	II	Extracted SA-50EE + decylamine	100	23.2	n.a.
SA-124**	II	SA50EE+ diethanolamine (2 to 1)	60 60R 60R+moisture 60R+moisture*	32.4 32 31.5 35	0.52 0.51 0.51 0.56
SA-127**	II	SA50EE+ diethanolamine (2 to 2)	60 60R 60R+moisture*	55 54 55	0.56 0.54 0.56
SA-131**	II	SA50EE+ diethanolamine (2 to 3)	60 60R	66.8 65	0.60 0.59
SA-126	II	SA50EE+ N-methyldiethanolamine	60 60R 60R+moisture*	9 8.5 9	0.23 0.22 0.23
HMS	III-1	Amine-templated	100	9.9	0.11
SA-117-amine	I-2	Grafted propylamine	100 100R 100R+moisture*	13 11.7 14.4	0.37 0.33 0.41
SA-128	I-2	Grafting of N-[3-(trinethoxysilyl)propyl]-ethylenediamine on MCM-41	100 100R	22 21	0.41 0.39
SA-129	I-2	Grafting of N,N-dimethylaminopropyltrimethoxysilane on MCM-41	100	2.5	low
SA-130	I-2	Grafting of N-phenylaminopropyltrimethoxysilane on MCM-41	100	3	low

\* Water vapor (saturated at 12°C) was brought to contact with sample for 1 h before CO<sub>2</sub> adsorption.

\*\* Increasing amounts of diethanolamine were adsorbed.

R = regenerated

5

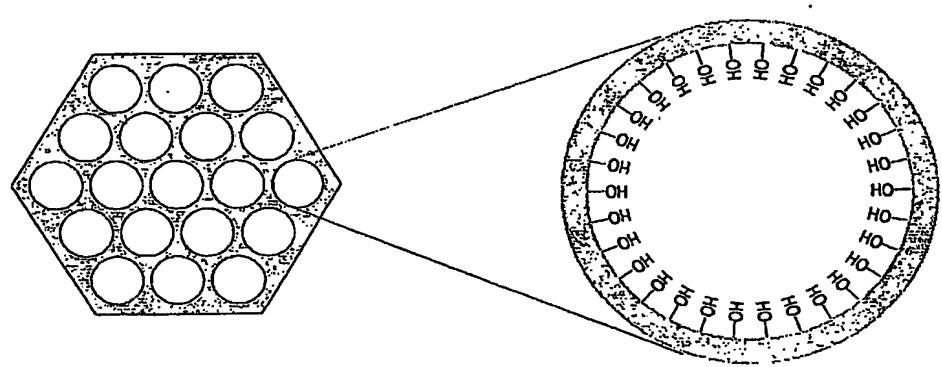
The invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention, and all such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the following claims.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR  
PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

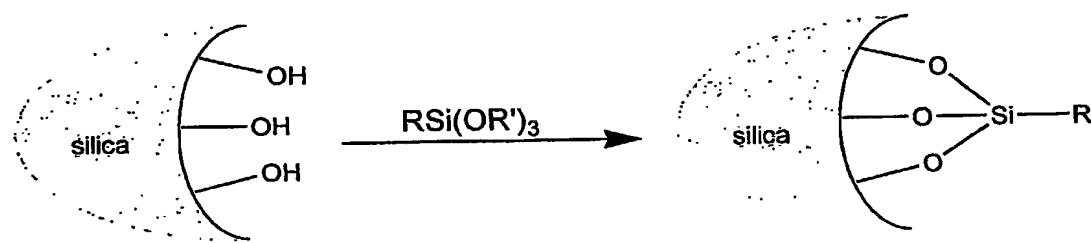
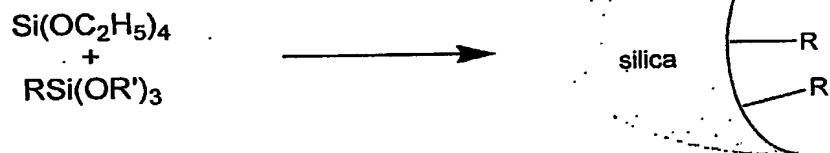
1. A water-tolerant, regenerable adsorbent comprising surface or framework amine-functionalised mesoporous silica or organosilica, for use in a CO<sub>2</sub> dry scrubbing process.

**MODIFIED ADSORBENT FOR DRY SCRUBBING AND USE THEREOF****ABSTRACT**

The present invention provides an amine functionalised adsorbent for use in dry scrubbing process. The adsorbent comprises amine functionalised mesoporous silica in which the amine groups are present at or near the surface of the silica, including within the pore walls and channels of the silica. The present invention further provides methods of preparing the adsorbent and of using the adsorbent for the adsorption of CO<sub>2</sub> and/or other acid gases.

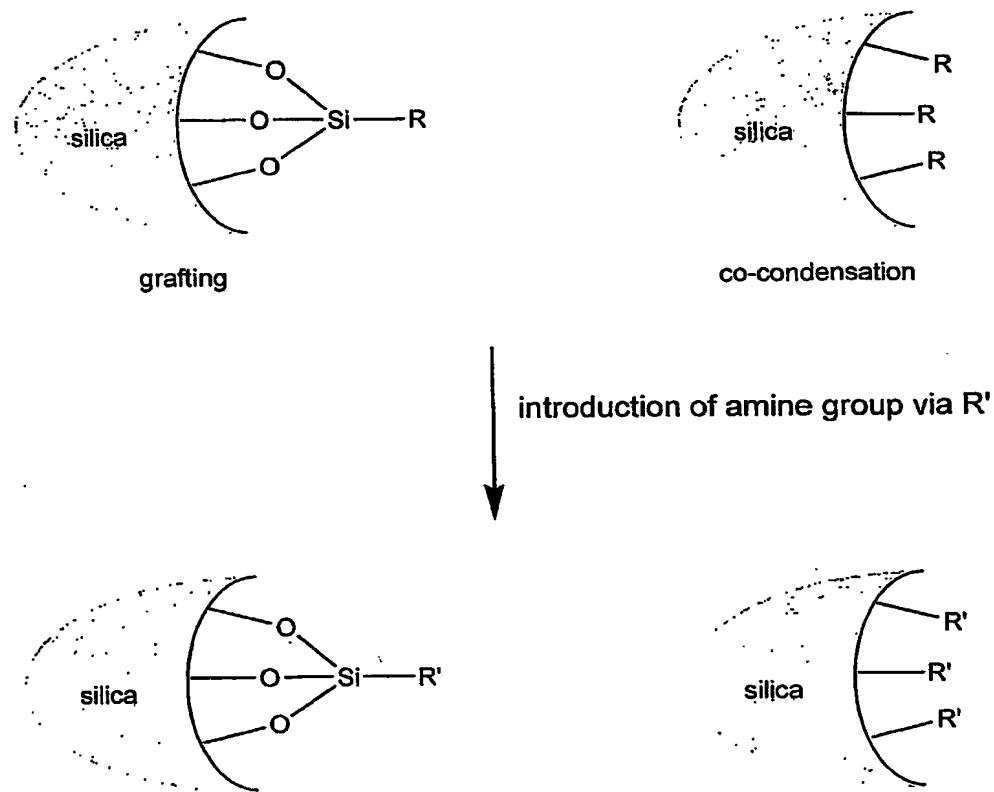


**FIGURE 1**

**GRAFTING****CO-CONDENSATION**

$\text{R}$  = substituent containing one or more amine group

**FIGURE 2**



R = substituent containing suitable reactive group(s)  
R' = substituent containing one or more amine group

**FIGURE 3**

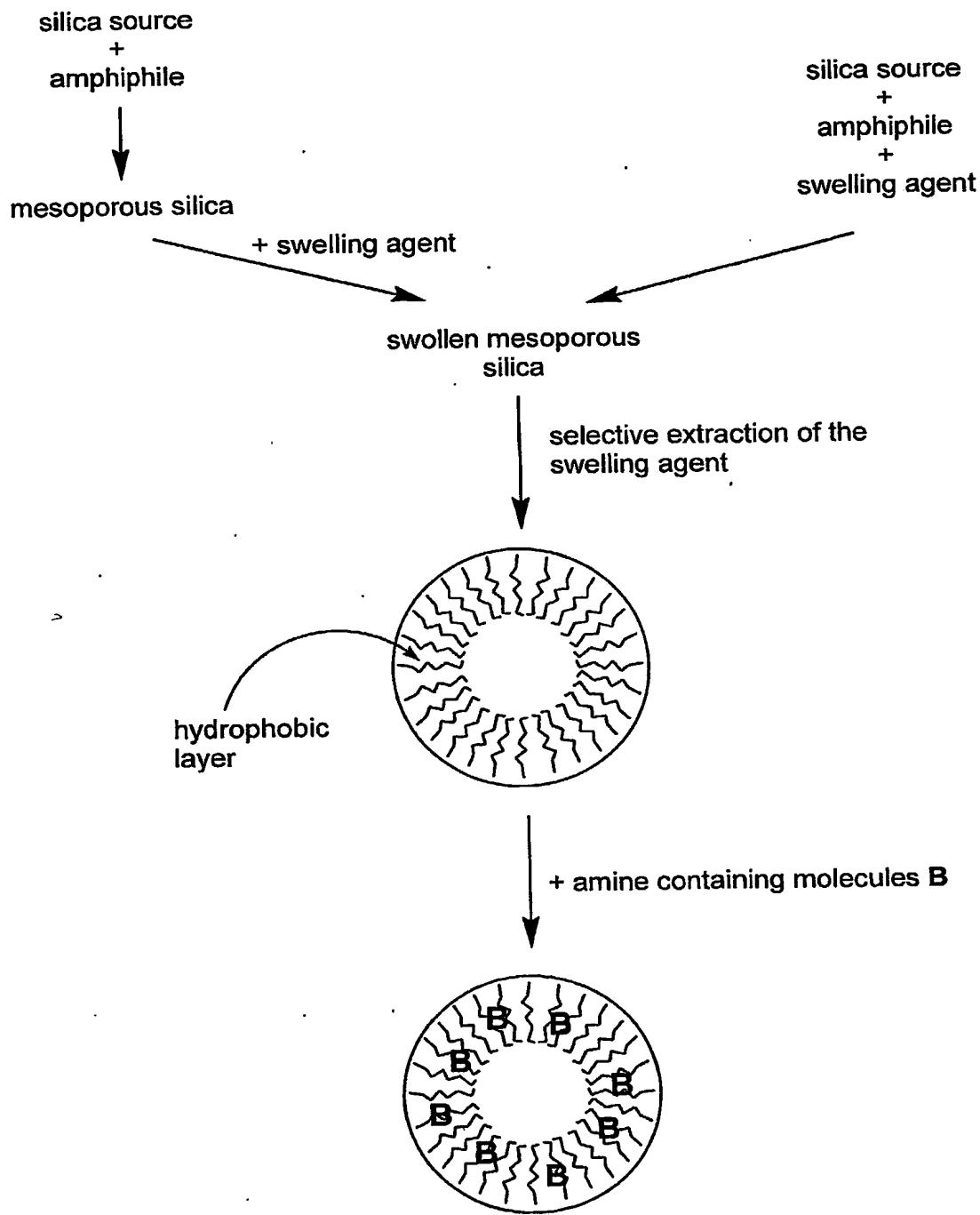
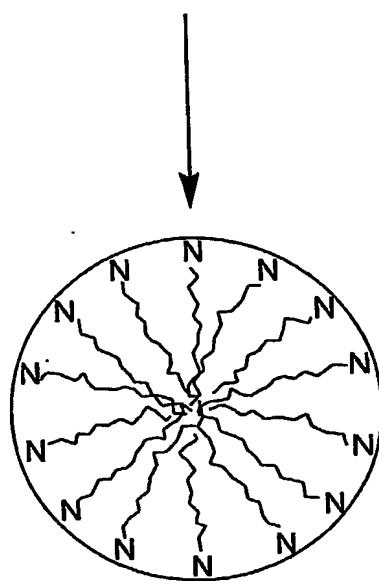
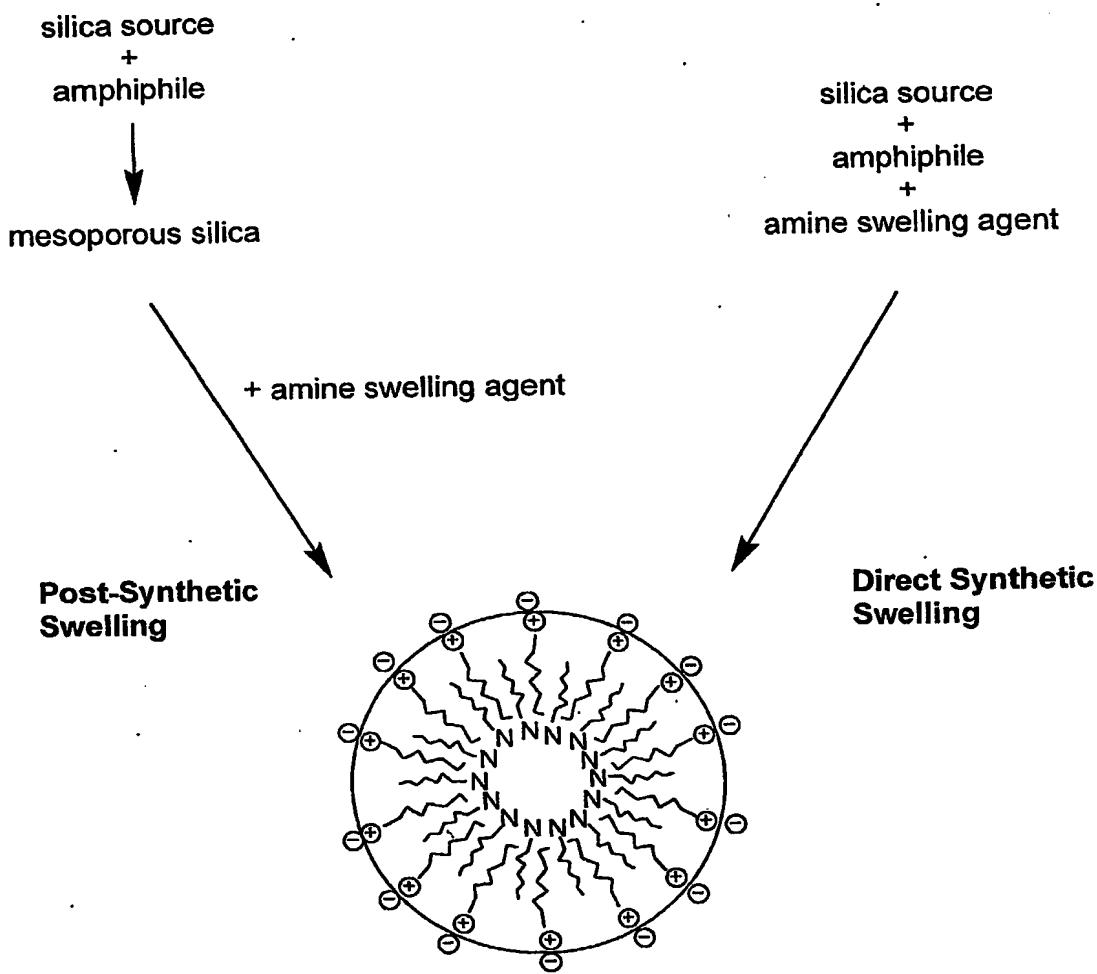


FIGURE 4

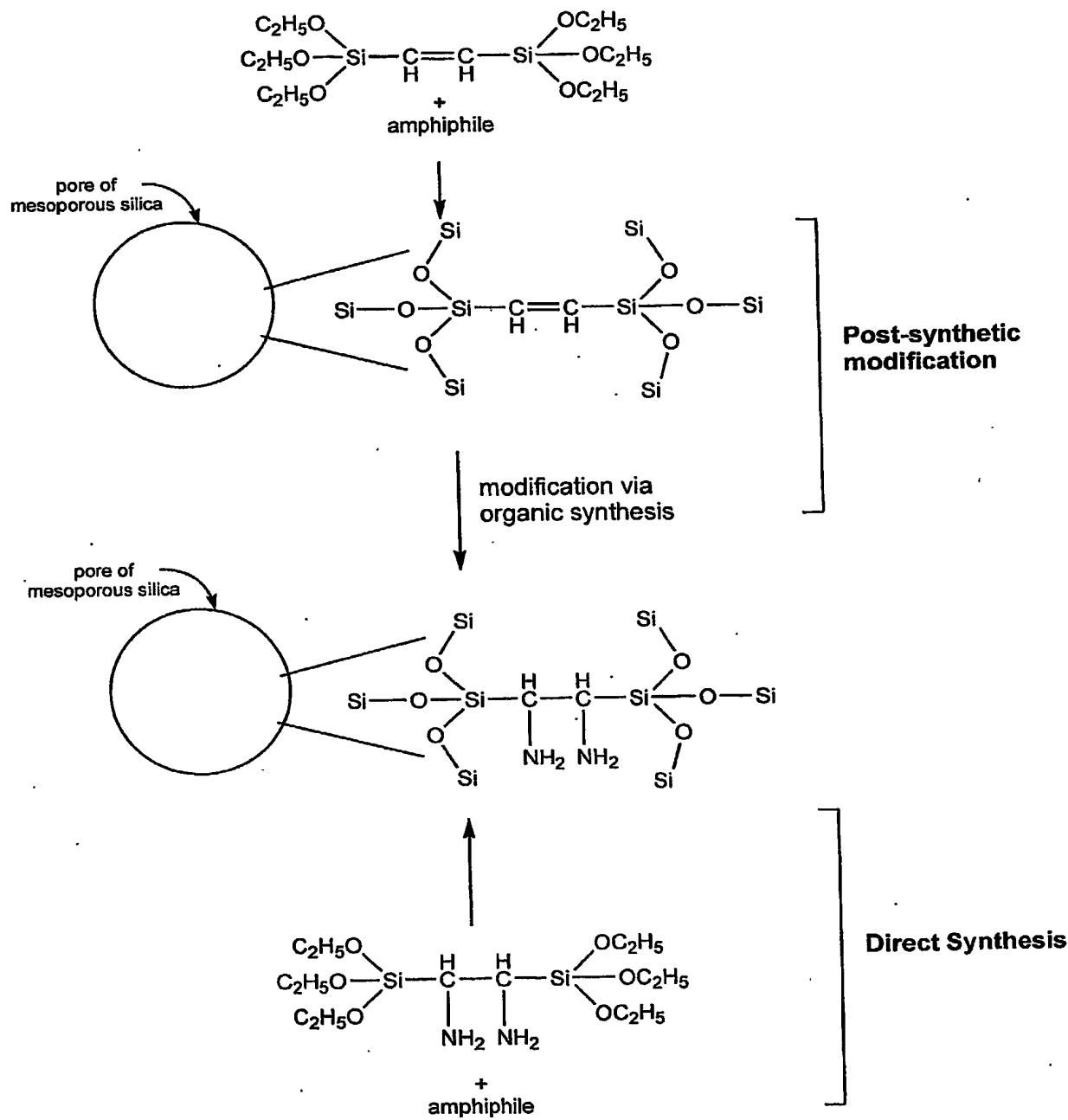
silica source  
+  
alkylamine



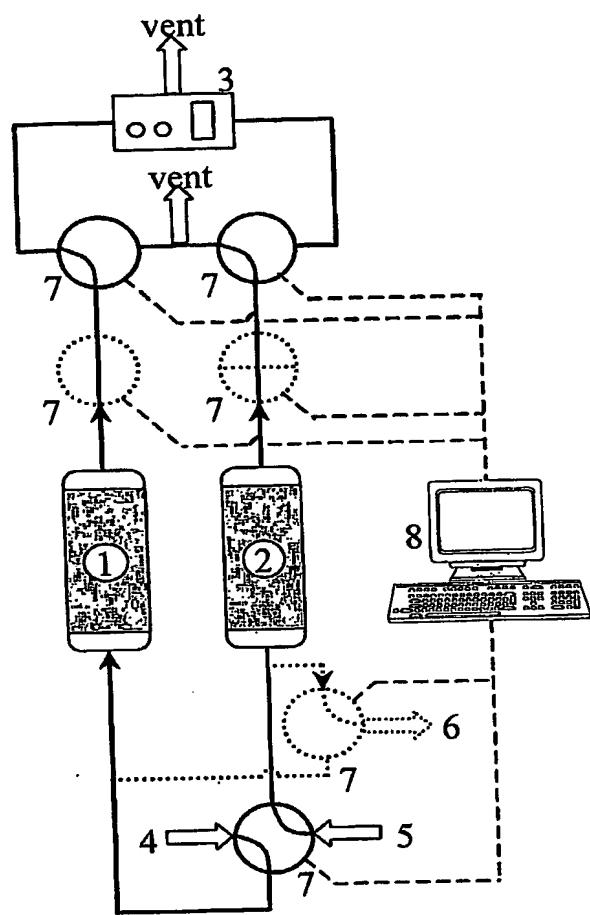
**FIGURE 5**



**FIGURE 6**



**FIGURE 7**



**FIGURE 8**

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